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<b>(54) Title:</b> PROCESS FOR PREPARING RETORT-STABLE, EXTRUDED, SHAPED FOOD PIECES <b>(57) Abstract</b> <p>The present invention relates to a process for preparing a retort-stable, shaped food piece, said process comprising: (a) preparing a premixture comprising (1) from about 15 % to about 65 % by weight protein, (2) from about 15 % to about 65 % by weight starch, (3) from 0 % to about 9 % by weight fat, (4) from 0 % to about 0.7 % by weight added sulfur, (5) from 0 % to about 2 % by weight dicalcium phosphate, wherein the weight percentage of the premixture components are expressed as a percentage of the premixture; (b) combining the premixture with water to form a secondary mixture, wherein the ratio of premixture to water is in the range of from about 1.6:1 to about 4:1; (c) mixing the secondary mixture for a period of time sufficient to obtain a substantially uniformly mixed dough and under conditions such that the temperature of the secondary mixture and uniformly mixed dough in the mixing operation are maintained in the range of from about 15 °C to about 45 °C; and (d) extruding the uniformly mixed dough into a desired shaped piece, wherein the extrusion is carried out in conjunction with low specific mechanical energy and high pressure conditions, and under conditions such that the temperature of the uniformly mixed dough in the extrusion operation is in the range of from about 40 °C to about 100 °C, and wherein said shaped piece is cohesive and maintains its shape when retorted. The present invention further relates to a piece prepared by the above-described process.</p>		

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5           Process for preparing retort-stable, extruded, shaped food pieces.

10                           FIELD OF INVENTION

          The present invention relates to a process for preparing a retort-stable, extruded, shaped food piece which is cohesive and maintains its shape when retorted. The present invention further relates to the retort-stable, extruded, shaped food  
15 piece prepared by the process of the present invention.

BACKGROUND OF INVENTION

          Pet owners typically have a great deal of affection for their pets. Many, in fact, consider their pets to be members of their families, and treat them accordingly by indulging  
20 them to a great degree. One of the ways owners indulge their pets is by the food they purchase for them. In this context, many owners derive pleasure from feeding their pets foods which contain shaped food pieces which the owner identifies with the particular type of pet. An example of this would be  
25 a bone-shaped food piece in a dog food.

          Of course, these shaped food pieces must also contribute to satisfying the nutritional requirements for the particular pet. To accomplish this, the shaped pieces are preferably prepared from proteinaceous and farinaceous material. The  
30 term proteinaceous material refers to glutens such as wheat gluten, corn gluten, rice gluten, and other types of cereal grain glutens known to those skilled in the art; proteinaceous material obtained from other sources such as defatted oil seed

protein material; dried eggs; whole corn; wheat germ meal; dehulled soy meal; meat and bone meal; and other known proteinaceous sources. The term farinaceous material refers to cereal flours such as wheat flour, corn flour, rice flour, oat flour, and other types of cereal flours known to those skilled in the art; ground hard wheat; ground whole corn; and other types of ground cereal-based grain material.

One problem in preparing such extruded, shaped pieces is that many pet foods have to undergo the extreme processing conditions of a retort sterilization procedure. For certain shaped proteinaceous materials, such as meat analogs, this is not a concern. These meat analogs retain their analog properties even when subjected to a retort operation. However, these meat analogs are structurally different than the shaped pieces of the present invention in that they are typically prepared from texturized vegetable protein (TVP) and may have a striated texture. By "striated texture" it is meant that the shaped piece tends to have a texture analogous to muscle striations. This striated texture allows the shaped piece to be easily torn apart along the striations, and as such the piece does not have to maintain a distinct and definite shape when subjected to a retort operation.

The extruded shaped pieces of the present invention do not have such a striated texture, however, but instead are, for the most part, cohesive. Until now, extruded shaped pieces having a cohesive texture like those of the present invention could not withstand the extreme conditions of a retort operation, but would typically dissolve when retorted.

This would be undesirable since the shaped piece would not maintain its original shape and form, but would be unrecognizable.

Thus, shaped food pieces having the cohesive consistency of the shaped pieces of the present invention are useful only when they are retort-stable, i.e., do not dissolve upon hydration and/or retorting, but maintain their desired shape. The present invention provides such a piece, as well as a process for its preparation.

#### BACKGROUND ART

There are numerous processes known in the art for producing shaped, extruded, edible proteinaceous products.

U.S. Patent 3,968,268, issued July 6, 1976 to Sair et al., discloses a process for producing hydratable, translucent to glassy, proteinaceous products, and the resulting products themselves. In the claimed process a water-moistened, edible proteinaceous material having at least about 40% by weight protein, on a dry weight basis, and an effective amount of water, within the range of about 10 to 50%, is subjected to working under effective mechanical pressure with added heat sufficient to convert it to a hot, moist, plastic extrudable mass. This hot, plastic mass is extruded through and from a length of a temperature controlled, elongated die under non-puffing conditions. The extruded product is unpuffed, substantially homogeneous, translucent to glassy, and characterized by having texture and retaining its structural integrity under retorting conditions. This product is alleged to be pleasing in the mouth and have protein cell bodies with

the pleasing feel, firmness, structure, texture, coarseness, or bite characteristics found in uncooked or cooked food products.

5       Sair et al. also teach that in their process the proteinaceous material must be heated to a sufficiently high temperature to retain retort stability. Specifically, they teach that extruded proteinaceous materials which are extruded at temperatures of 180°F., 210°F., and 230°F., completely disintegrate when subjected to retorting. This is contrary to  
10       what has been found in the present invention, where the products are shaped and formed at low dough temperatures and maintain their shape when retorted.

      U.S. Patent 3,965,268, issued June 22, 1976 to Stocker et al., refers to an expanded protein product comprising a  
15       sulfur-containing organic compound. Stocker et al. claim a method of preparing an expanded edible protein product having an open, cellular structure, the method comprising forming an admixture of proteinaceous material having a protein content of at least about 30% by weight, from about 0.05% to about  
20       2.0% by weight of said proteinaceous material of a sulfur-containing organic compound selected from the group consisting of cysteine hydrochloride, D,L-methionine, sodium lignosulfonate, thiamine mononitrate, calcium thioglycollate, and mixtures thereof, and water in an amount sufficient to  
25       result in a moisture content of 15% to about 50% by weight of said admixture; heating the mix to a temperature above about 220°F; mechanically working the heated mix at a pressure substantially above atmospheric pressure; and expanding the

mix by suddenly releasing the pressure. The expanded product has a crisp, crunchy texture which lends itself to use in a large number of foodstuffs, for example snack items.

As can be seen, the product of the process taught by Stocker et al. has a different texture than the shaped edible piece of the present invention. Furthermore, the process taught by Stocker et al. includes a heating step which is not required in the process of the present invention.

As already stated herein, it is also known to make a striated, texturized shaped meat analog. This technology uses a vegetable protein, or extract, along with a sulfur-containing compound, typically a sulfur-containing amino acid or pure sulfur itself, to make the striated, texturized piece. An extrusion process operated under high shear and temperature conditions is typically used to manufacture this meat analog. The high shear and temperature conditions facilitate the cross-linking of the vegetable proteins.

The resulting extruded meat analog is typically very porous, and upon hydration expands to several times its dry weight and size. The hydrated meat analog is also porous and is spongy to the touch and chew. After retorting, the hydrated and retorted meat analog is spongy and soft. The meat analog is easily torn apart following retorting, due to its striated structure.

As can be seen, there is nothing in the art which teaches the shaped piece prepared by the process of the present invention. It is therefore an object of the present invention to provide a process for preparing such a shaped food piece

which is cohesive and maintains a definite and distinct shape and integrity when hydrated and/or retorted.

It is another object of the present invention to provide an edible, shaped food piece which is cohesive and maintains a definite and distinct shape and integrity when hydrated and/or  
5 retorted.

These objects are accomplished by the invention described herein.

Unless otherwise specified, the weight percentages provided herein for the components of the premixture are on a  
10 wet basis.

#### SUMMARY OF THE INVENTION

The present invention relates to a process for preparing a cohesive, retort-stable, shaped food piece, said process  
15 comprising:

(a) preparing a premixture comprising

- (1) from about 15% to about 65% by weight protein,
- (2) from about 15% to about 65% by weight starch,
- (3) from 0% to about 9% by weight fat,
- 20 (4) from 0% to about 0.7% by weight added sulfur,
- (5) from 0% to about 2% by weight dicalcium phosphate, wherein the weight percentage of the premixture components are expressed as a percentage of the premixture;

25 (b) combining the premixture with water to form a secondary mixture, wherein the ratio of premixture to water is in the range of from about 1.6:1 to about 4:1;



(c) mixing the secondary mixture for a period of time sufficient to obtain a substantially uniformly mixed dough and under conditions such that the temperature of the secondary mixture and uniformly mixed dough in the mixing operation are maintained in the range of from about 15°C to about 45°C; and

(d) extruding the uniformly mixed dough into a desired shaped piece, wherein the extrusion is carried out in conjunction with low specific mechanical energy and high pressure conditions, and under conditions such that the temperature of the uniformly mixed dough in the extrusion operation is in the range of from about 40°C to about 100°C, and wherein said shaped piece is cohesive and maintains its shape when retorted.

The present invention further relates to a piece prepared by the above-described process.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises a process for preparing a retort-stable, shaped food piece. The piece maintains its shape when hydrated and retorted, e.g., if the piece is originally formed in a bone shape, the hydrated piece will maintain the bone shape and the retorted piece will maintain the bone shape.

In the process of the present invention a premixture is initially prepared. The premixture comprises from about 15% to about 65%, preferably from about 15% to about 35%, more preferably from about 20% to about 30% by weight protein; from

about 15% to about 65%, preferably from about 25% to about 60%, more preferably from about 30% to about 55% by weight starch; from 0% to about 9%, preferably from about 1% to about 8%, more preferably from about 3% to about 6% by weight fat; from 0% to about 0.7%, preferably from about 0.01% to about 0.5%, more preferably from about 0.1% to about 0.2% by weight added sulfur; and from 0% to about 2%, preferably from about 0.1% to about 1% dicalcium phosphate.

The protein present in the premixture of the present invention may be derived from any source known to those skilled in the art, and is preferably derived from wheat gluten. It is believed that other protein sources, such as corn gluten, may work in the present invention as well. Examples of other protein sources believed to be useful in the present invention include, but are not limited to, those protein sources listed in Table I below. Table I also includes an approximate description of the amount of protein, starch (also stated as "carbohydrate"), fat, and moisture each protein source can contribute to the premixture. These protein sources may also be combined with each other in the premixture.

Table I: Sources of Protein and Starch that may be used in premixture:

INGREDIENT	MOISTUR%	PROT %	FAT %	CARBOH %
CRACKD PEARLED BARLEY	11.194	12.584	1.724	70.987
CORN FLOUR	9.438	7.339	2.111	79.202
CORN GERM MEAL	10.631	12.077	0.919	60.732
CORN STARCH	9.850	2.517	0.195	87.125
CORN YELLOW	14.201	8.692	3.600	69.807

CORN	14.500	8.110	3.600	70.290
OAT FLOUR	8.650	15.300	6.100	66.876
FEEDING OATMEAL	7.507	14.427	7.700	66.416
CORN GLUTEN MEAL	10.841	61.694	5.272	19.619
BREWERS RICE	11.559	9.027	0.610	76.704
RICE HULLS	9.162	3.405	8.600	22.966
CORN	12.431	8.727	4.730	70.642
GROUND SOYBEAN HULLS	9.962	13.476	1.200	36.817
SOYBEAN MEAL	11.652	45.290	2.575	30.626
DEHULL SOY MEAL	10.954	48.818	2.820	28.339
SOY FLOUR	5.251	53.650	2.551	34.328
SOY FLOUR	5.505	53.357	1.397	29.583
SOY PROTEIN CONC.	6.534	66.261	0.568	17.908
SOYBEAN GRITS - 50%	7.945	52.901	1.100	28.647
SOY FLOUR	5.799	52.693	2.469	30.186
TEX SYBN FL	7.850	50.000	1.000	31.950
TVP	8.980	51.400	1.680	29.080
WHEAT	12.168	11.394	1.600	72.506
WHEAT FEED FL	12.684	14.349	2.420	68.010
WHEAT FEED FL	11.677	11.823	1.865	72.623
WHEAT FEED FL	5.881	13.709	2.757	75.756
WHEAT BRAN	13.802	17.473	3.274	49.159
WHEAT GERM MEAL	12.786	27.136	7.669	44.935
WHEAT MIDDLINGS	12.576	16.337	3.591	54.452
WHEAT	10.195	13.856	2.960	68.526
PELLETED WHEAT MIDDS	12.042	15.975	3.591	55.348
WHEAT FEED FL	10.990	15.030	3.390	67.733
WHEAT FEED FL	11.984	17.306	3.390	64.716
WHEAT GLUTEN	9.100	78.990	0.818	9.819

Wheat gluten is the preferred source of protein in the premixture of the present invention. This is because wheat gluten has a relatively high protein concentration (79%) and is therefore a good protein source.

Wheat gluten is a concentrated natural protein in the form of a light tan powder having a bland taste and aroma. Wheat gluten is known to consist mainly of gliadin (prolamine) and glutenin (glutelin), which are the principle cereal proteins, together with other components of the endosperm

cell. Wheat gluten is separated from wheat flour by a washing method known to those skilled in the art.

The precise amount of any particular protein source used to prepare the premixture of the present invention will be that amount necessary to provide a protein content in the premixture in the range of from about 15% to about 65% by weight, and will be dependent upon the particular protein source utilized and the protein content of the particular source. The preferred wheat gluten, which has a protein content of 79% by weight, will comprise from about 20% to about 80%, preferably from about 20% to about 40%, more preferably from about 25% to about 35% by weight of the premixture.

The gluten protein source may be provided to the premixture in the form of isolated gluten added to the premixture, gluten inherent in the starch source present in the premixture, and mixtures thereof.

The starch source used in the present invention may be derived from any starch source known to those skilled in the art, including, but not limited to, cereal flours obtained from known grains; ground hard wheat; ground whole corn; and other types of ground cereal-based grain material. Examples of flours useful in the present invention include, but are not limited to, wheat flour, corn flour, oat flour, along with other types of cereal flours known to those skilled in the art, and mixtures thereof, with corn flour being preferred.

As with the protein source, the precise amount of any particular starch source used in preparing the premixture of

the present invention will be that amount necessary to provide a total starch content in the premixture in the range of from about 15% to about 65% by weight, and is dependent upon the particular type of starch source being utilized and the starch content of the starch source. For example, the preferred corn flour has a starch content of about 79% by weight. When this preferred corn flour is used, the premixture comprises from about 20% to about 80%, preferably from about 30% to about 75%, more preferably from about 35% to about 65% by weight corn flour.

The exact amounts of any particular protein and/or starch source required to prepare the premixture of the present invention can be calculated by using the approximate concentrations of protein and starch contained in the specific type of ingredient, as stated in Table I, and determining the amount of ingredient needed to achieve a total premixture concentration in the above specified ranges.

The fat which may be added to the premixture of the present invention may be obtained from any fat source known to those skilled in the art. Examples of fat sources useful in the present invention include, but are not limited to, choice white grease, beef tallow, soy oil, corn oil, vegetable oil, and mixtures thereof, with choice white grease being the preferred fat source.

The amount of a particular fat source that must be used in the premixture is that amount necessary to provide a total fat content in the premixture in the range of from 0% to about 9%, preferably from about 1% to about 8%, more preferably from

about 3% to about 6% by weight. Of course, the required amount of a particular fat source necessary to achieve this will vary for differing fat sources. However, this is something one skilled in the art can determine. When the preferred choice white grease is used as the fat source, the premixture comprises from 0% to about 9%, preferably from about 1% to about 8%, more preferably from about 3% to about 6% by weight choice white grease.

When fat is included in the premixture of the present invention it facilitates the process of the present invention by lubricating the material flow through the extrusion operation, thereby lowering shear and energy transfer to the product.

The sulfur which may be added to the premixture of the present invention may be in the form of pure sulfur or either as an organic or inorganic sulfur-containing compound. This sulfur is considered "added sulfur" and is added to the premixture separately from the other premixture ingredients and in a manner sufficient to contribute the specified amount of sulfur to the premixture. Sulfur may also be present in the other premixture ingredients (e.g., gluten, flour, etc.), but any such amounts are typically not significant and are not considered when determining the amount of sulfur added to the premixture.

Any type of sulfur-containing compound useful in the preparation of edible foodstuffs may be used in preparing the premixture of the present invention. Examples of useful sulfur-containing organic compounds include, but are not

limited to, sulfur-containing amino acids, lower alkyl mercaptans, lower alkyl sulfides, lower alkyl disulfides, thioacids, and other compounds, for example thiamine, may be employed. Among these, compounds such as cysteine, cystine, methionine, thiodipropionic acid, thioglycollin, thiamine, lignosulfonic acid, and their salts are preferred, with methionine being most preferred.

The amount of a particular sulfur source that must be used in the premixture is that amount sufficient to provide a total added sulfur content in the premixture in the range of from 0% to about 0.7%, preferably from about 0.01% to about 0.5%, more preferably from about 0.1% to about 0.2% by weight of the premixture. Of course, the required amount of a particular sulfur source necessary to achieve this will vary for differing sulfur sources, although falling within the broad range specified above, and will be appreciated by one skilled in the art. When the preferred methionine is used as the sulfur source, it comprises from 0% to about 2%, preferably from about 0.1% to about 1%, more preferably from 0.2% to 0.5% by weight of the premixture.

The dicalcium phosphate, when added to the premixture of the present invention, comprises from 0% to about 2%, preferably from about 0.1% to about 1% by weight of the premixture.

Other optional ingredients which may be added to the premixture of the present invention include, but are not limited to, meat and bone meal, edible fiber sources,

nutritional supplements, coloring agents, and flavoring agents.

When such optional ingredients are added to the premixture, the levels at which they are added will vary depending upon the particular optional ingredient. When meat and bone meal is included in the premixture it typically comprises from 0% to about 50%, preferably from 1% to about 30%, more preferably from about 2% to about 15% by weight of the premixture.

When adding the fat, sulfur, dicalcium phosphate, and other optional ingredients, care must be taken to avoid adding amounts of such ingredients which may disrupt the formation of a gluten matrix. If such disruption occurs, then retort stability may be adversely affected.

Coloring agents and flavoring agents are added to the premixture at levels necessary to impart the desired flavor and color to the final product, which will be dependent upon the preferences of the particular formulator. Such coloring and flavoring agents are typically added to the premixture at levels of less than 1% by weight.

The premixture is next combined with water to form a secondary mixture. The ratio of the premixture to water is in the range of about 1.6:1 to about 4:1, preferably from about 1.65:1 to about 2.5:1, more preferably from about 1.65:1 to about 1.85:1.

Any type of water may be used to form the secondary mixture of the present invention, i.e., deionized water, purified water, distilled water, tap water, etc. Of course,



care should be taken to ensure that the water does not contain any impurities that may have an adverse effect on the final shaped piece produced in the present invention, i.e., particulate matter that might interrupt the gluten structure and adversely affect retort stability.

After the secondary mixture is prepared, it is mixed for a period of time sufficient to obtain a substantially uniformly mixed dough. Care must be taken to avoid mixing the secondary mixture past the point of minimum mobility or the dough (gluten structure) breaks down, and the resulting piece will not be retort stable. The minimum mobility of the secondary mixture can be determined by one skilled in the art.

The secondary mixture may be mixed by any method and/or apparatus known to those skilled in the art. Examples of mixing methods and/or apparatus useful in the present invention include, but are not limited to, a paddle mixer, a ribbon mixer, and a Hobart mixer (auger mixer), with a ribbon mixer being preferred.

The secondary mixture is mixed under conditions such that its temperature and the temperature of the resulting uniformly mixed dough are maintained in the range of from about 15°C to about 45°C, preferably from about 20°C to about 30°C, more preferably from about 20°C to about 25°C.

The length of time necessary for mixing the secondary mixture to obtain the substantially uniformly mixed dough will depend upon the method of mixing used. When a ribbon mixer is used, the secondary mixture is typically mixed for a period of time in the range of from about 2 to about 10 minutes,

preferably from about 3 to about 8 minutes, more preferably from about 4 to about 6 minutes.

After the substantially uniformly mixed dough is prepared, it is extruded into the desired shaped piece. It is  
5 important that this extrusion take place in conjunction with low specific mechanical energy and under high pressure conditions. The low specific mechanical energy and high pressure conditions act in combination to provide the structural bonding necessary to have a retort-stable, final  
10 shaped piece.

The extrusion operation is carried out in conjunction with specific mechanical energy in the range of from about 6 watt·hr/kg. to about 70 watt·hr/kg., preferably from about 6 watt·hr/kg. to about 50 watt·hr/kg., more preferably from  
15 about 6 watt·hr/kg. to about 35 watt·hr/kg., and under a pressure of at least about 400 psig, preferably at least about 500 psig, more preferably at least about 600 psig. If the pressure under which the extrusion takes place is too low, a final cohesive shaped piece will not be produced, but instead  
20 discreet separate individual particles will result from the extrusion. Furthermore, even if the pressure is sufficient to provide a uniform, solid, discreet, shaped piece, it still must be high enough to allow for some expansion of the uniformly mixed dough after the extrusion pressure is  
25 released. By this it is meant that there must be sufficient pressure in the extrusion operation that when the pressure is released, the shaped dough product will have a slight expansion due to release of the pressure alone. The expansion

is not due to any gas evolved after the pressure release or any other internal forces, other than the plastic reformation of the shaped product material.

It is also important that the extrusion take place under conditions such that the temperature of the uniformly mixed dough remains in the range of from about 40°C to about 100°C, preferably from about 40°C to about 90°C, more preferably from about 45°C to about 90°C, still more preferably from about 60°C to about 80°C. The specific mechanical energy and pressure will contribute to the increase in temperature of the substantially uniformly mixed dough as it is being extruded into the desired shaped piece. However, care should be taken to minimize the temperature rise during the extrusion of the dough in order to minimize gelatinization of the dough and keep the dough temperatures within the ranges specified herein.

Although gelatinization of the starch is minimized, some gelatinization is necessary to form the desired shaped piece. However, if there is too much gelatinization the formed piece becomes highly hydrophilic and is not retort stable. The correct degree of gelatinization will provide a product which is neutral to hydrophobic. It is also possible that an overly gelatinized piece will form an expanded cell structure, which can cause the shaped piece to lack retort integrity as well.

The temperature of the substantially uniformly mixed dough is also kept low to avoid generating steam during extrusion and causing the piece to have an expanded cell structure. If any steam is generated, then when the pressure

is released during the extrusion operation it is possible that the steam will expand the shaped piece, causing the shaped piece to have an undesirable texture and lack retort integrity. All of these problems can be avoided by  
5 maintaining the temperature of the dough below its gelatinization point.

Cooling of the extruder maybe necessary to control the dough temperature if the specific mechanical energy causes the temperature to rise too high. However, this is unlikely under  
10 the low specific mechanical energy conditions under which the extrusion is carried out.

The extruder is preferably operated at a speed in a range of from about 40 to 60 RPM, more preferably from about 45 to about 60 RPM, still more preferably from about 50 to about 60  
15 RPM; the pressure at the exit of the extruder is at least about 400 psig, preferably at least about 500 psig, more preferably at least 600 psig; and the dough is preferably extruded at a rate of 100 to 300 kg. dough per hr., preferably from about 100 to about 275 kg. dough per hr., more preferably  
20 from about 100 to about 250 kg. dough per hr.

In the present invention it has been found that a 4" diameter Bonnot 5-zone extruder is a preferred extruder. While the reason for this preference is not exactly known, it is believed that the Bonnot extruder has a particularly  
25 desirable screw profile for use in the process of the present invention. This extruder is available from The Bonnot Company, located in Uniontown, Ohio.

While not intending to be bound by theory, it is surprising and unexpected that the protein and starch, and especially protein in the form of wheat gluten and starch in the form of corn flour, when processed under the low specific mechanical energy, low dough temperature, and high pressure extrusion conditions of the process of the present invention produces a cohesive shaped piece which maintains its distinctive definitive shape upon hydration and retort. This is especially unexpected when it is considered that the product of the present invention is prepared using a low specific mechanical energy, low temperature, high pressure extrusion. As already stated herein, the prior art teaches that high temperature extrusion is necessary to obtain a retort-stable piece. The art teaches that extrusion temperatures of at least about 250°F are necessary for preparing a retort-stable product, and that retorted, proteinaceous extruded products which are extruded at temperatures of 180°F, 210°F, and 230°F dissolve when retorted.

A preferred process of the present invention comprises:

(a) preparing a premixture comprising

- (1) from about 25% to about 35% by weight wheat gluten,
- (2) from about 35% to about 65% by weight corn flour,
- (3) from about 3% to about 6% by weight choice white grease,

(4) from about 0.2% to about 0.5% by weight methionine,

(5) from about 0.1% to about 1% by weight dicalcium phosphate;

5 (b) combining the premixture with water to form a secondary mixture, wherein the ratio of premixture to water is in the range of from about 1.65:1 to about 1.85:1;

10 (c) mixing the secondary mixture in a ribbon mixer for a period of time in the range of from about 4 to about 6 minutes, thereby obtaining a substantially uniformly mixed dough, wherein said mixing is carried out under conditions such that the temperature of the secondary mixture and uniformly  
15 mixed dough in the mixing operation are maintained in the range of from about 20°C to about 25°C; and

(d) extruding the uniformly mixed dough into a desired shaped piece, wherein the extruder is operated at a speed in the range of from about 50 to 60 RPM, the  
20 dough exit temperature is in the range of from about 60°C to about 80°C, the exit pressure is at least 600 psig, and the specific mechanical energy provided by the extruder is in the range of from about 6 watt·hr./kg. to about 35 watt·hr./kg.

25 The present invention also relates to a cohesive, retort-stable, shaped food piece prepared by the method comprising:

(a) preparing a premixture comprising

(1) from about 15% to about 65% by weight protein,

(2) from about 15% to about 65% by weight starch,  
(3) from 0% to about 9% by weight fat,  
(4) from 0% to about 0.7% by weight added sulfur,  
(5) from 0% to about 2% by weight dicalcium  
phosphate, wherein the weight percentage of the  
premixture components are expressed as a  
percentage of the premixture;

(b) combining the premixture with water to form a  
secondary mixture, wherein the ratio of premixture  
to water is in the range of from about 1.6:1 to  
about 4:1;

(c) mixing the secondary mixture for a period of time  
sufficient to obtain a substantially uniformly mixed  
dough and under conditions such that the temperature  
of the secondary mixture and uniformly mixed dough  
in the mixing operation are maintained in the range  
of from about 15°C to about 45°C; and

(d) extruding the uniformly mixed dough into a desired  
shaped piece, wherein the extrusion is carried out  
in conjunction with low specific mechanical energy  
and high pressure conditions, and under conditions  
such that the temperature of the uniformly mixed  
dough in the extrusion operation is in the range of  
from about 40°C to about 100°C, and wherein said  
shaped piece is cohesive and maintains its shape  
when retorted.

The present invention is further illustrated, but not  
limited by, the following examples.

EXAMPLESExample 1

A premixture containing 0.33 lb. sorbic acid; 1 lb. hydrochloric acid; 1.33 lb. dried whole eggs; 1.67 lb. dicalcium phosphate; 48 lb. ground yellow whole corn; 14.3 lb. dehulled soy meal; 1 lb. wheat germ meal; 15.33 lb. hard wheat; 4 lb. degummed oil; and 13 lb. meat and bone meal is initially prepared and blended for 2 minutes in a Buffalo Mixer (which is a ribbon blender). Water is added to this blended premixture at a weight ratio of 2.2:1 (blended premixture:water) to prepare a wet mixture. The wet mixture is blended in the Buffalo Mixer for another 10 minutes to form a dough.

The dough is removed from the mixer fed to a 4 inch diameter, 5 zone Bonnot extruder using a "Bonnot #6" (designated by Bonnot) screw shaft. The exit of the extruder is fitted with a die consisting of a single rectangular opening (a "slit" shape) with the dimension of 1/8 inch width by 5/8" inch length.

The extruder is operated at 40 rpm (screw rotation speed) and the body of the barrels is jacketed with cold water in all 5 zones (numrating the zones starting from the feed inlet to the exit of the extruder). The dough is fed into the extruder at a rate as fast as the rotating screw can convey it away from the feed inlet (this is known as "choke-fed").

After operating for about 5 minutes the process reaches a state of equilibrium. The dough is fed at a rate of 200 kg. dough per hr. The exit temperature of the product is 170°F



(62°C) and the pressure, as measured at an outlet immediately before the die-assembly, is approximately 600 psig.

As the extrudate emerges from the die it is cut in pieces. The cutting speed is set sufficiently fast to produce cut pieces of thickness of approximately 1/2 to 1 inch long, resulting in rectangular pieces. The cut pieces are conveyed away from the pelletizer by a cool air stream which facilitates transfer and prevents the cut pieces from adhering to each other. The collected cut pieces are dried in a Proctor and Schwartz dryer for 2 hours until their overall moisture content is less than 12% w/w basis.

The dried cut pieces are placed in cans of pet food along with other components, such as meat pieces and gravy. The amount of cut pieces in each can is 3% and the gravy (which is essentially 95% water) comprises 50 wt. % of the can contents. The overall moisture content of the canned ingredients is approximately 80%. The cans are sealed and retorted at 250°F for 65 minutes. The resulting canned contents include "flat-shaped" extruded pieces. The cross sectional shape of the extruded pieces is essentially the same shape as the opening in the die. The "flat-piece" can be handled without losing its integrity.

#### Example 2:

A dry mixture consisting of 283 lb. wheat gluten, 318 lb. meat and bone meal, 353 lb. wheat flour, 60 lb. choice white grease, 21 lb. methionine, 21 lb. dicalcium phosphate, and 4 lb. of titanium dioxide is blended for 2 minutes in a Buffalo Mixer (which is a ribbon blender). To 250 lb. of this

mixture, 125 lb. of water is added. The "wet mixture" is then blended in the Buffalo Mixer for another 10 minutes.

The wet mixture ("the dough") is now removed from the mixer and ready to be fed to the extruder. The extruder used is a 4 inch diameter 5 zone Bonnot extruder using a "Bonnot #5" (designated by Bonnot) screw shaft. The exit of the extruder is fitted with a die having a single opening in the shape of a bone.

The extruder is operating at 57 rpm (screw rotation speed) and the body of the barrels is jacketed with cold water in the first two zones (numerationg the zones starting from the feed inlet to the exit of the extruder) and nothing jacketing the last 3 zones. The dough is fed into the extruder at a rate as fast as the rotating screw can convey it away from the feed inlet (this is also known as "choke-fed").

After operating for about 5 minutes at a rotating speed of 57 rpm and dough fed in continuously, the entire process has reached a state of equilibrium. The dough is being fed at about 300 kg/hr. The exit temperature of the product is 180°F (68°C) and the pressure, as measured at an outlet immediately before the die-assembly, is approximately 390 psig.

As the extrudate emerges from the die, it is pelletized by an attached multi-knife cutter. The kibble thus produced is then conveyed away from the pelletizer by a cool stream of air to facilitate transfer and to prevent the kibbles from adhering to each other. The collected kibbles are then dried in a Proctor and Schwartz dryer for 2 hours until the kibbles has reached an overall moisture of 8% w/w basis.

The dry kibble is now put into cans of pet foods along with other components, such as meat pieces and gravy. The amount of kibbles in each can is 3% and the gravy (which is essentially 95% water) is 50%; the overall moisture of the can content is 80%. The cans are sealed and retorted at 250°F for 65 minutes. The resulting retorted canned contents include the "bone-shaped" extruded pieces. The bone shape of the extruded pieces is essentially the same shape as the opening in the die. The "bone-piece" can be handled without losing its integrity.

Example 3:

A dry mixture consisting of 54 lb. wheat gluten, 128 lb. corn flour, 12 lb. choice white grease, 4 lb. dicalcium phosphate, and 4 lb. of methionine,, is blended for 2 minutes in a Buffalo Mixer (which is a ribbon blender). To this mixture, 100 lb. of water is added. The "wet mixture" is then blended in the Buffalo Mixer for another 10 minutes.

The wet mixture ("the dough") is now removed from the mixer and ready to be fed to the extruder. The extruder used is a 4 inch diameter 5 zone Bonnot extruder using a "Bonnot #5" (designated by Bonnot) screw shaft. The exit of the extruder is fitted with a die consisting of 9 circular openings and each opening has a diameter of 1/8 inch.

The extruder is operating at 50 rpm (screw rotation speed) and the body of the barrels is jacketed with cold water jacketing all 5 zones. The dough is fed into the extruder at a rate as fast as the rotating screw can convey it away from the feed inlet (this is also known as "choke-fed").

After operating for about 5 minutes at a rotating speed of 50 rpm and dough fed in continuously, the entire process has reached a state of equilibrium. The dough is being fed at about 250 kg/hr. The exit temperature of the product is 155°F (54°C) and the pressure, as measured at an outlet immediately before the die-assembly, is approximately 600 psig.

As the extrudate emerges from the die, it is pelletized by an attached multi-knife cutter. The cutting speed is set sufficiently fast to produce cut pieces of thickness of approximately 1/2 to 1 inch long. The kibble thus produced is then conveyed away from the pelletizer by a cool stream of air to facilitate transfer and to prevent the kibbles from adhering to each other. The collected kibbles are then dried in a Proctor and Schwartz dryer for 2 hours until the kibbles has reached an overall moisture of 10% w/w basis.

The dry kibble is now put into cans of pet foods along with other components, such as meat pieces and gravy. The amount of kibbles in each can is 3% and the gravy (which is essentially 95% water) is 50%; the overall moisture of the can content is 80%. The cans are sealed and retorted at 250°F for 65 minutes. The resulting retorted canned contents include the "bone-shaped" extruded pieces. The bone shape of the extruded pieces is essentially the same shape as the opening in the die. The "bone-piece" can be handled without losing its integrity.

CLAIMS

1. A process for preparing a retort-stable, shaped food piece, said process comprising:

- 5           (a) preparing a premixture comprising
- (1) from about 15% to about 65% by weight protein,
  - (2) from about 15% to about 65% by weight starch,
  - (3) from 0% to about 9% by weight fat,
  - (4) from 0% to about 0.7% by weight added sulfur,
  - 10           (5) from 0% to about 2% by weight dicalcium phosphate, wherein the weight percentage of the premixture components are expressed as a percentage of the premixture;
- 15           (b) combining the premixture with water to form a secondary mixture, wherein the ratio of premixture to water is in the range of from about 1.6:1 to about 4:1;
- 20           (c) mixing the secondary mixture for a period of time sufficient to obtain a substantially uniformly mixed dough and under conditions such that the temperature of the secondary mixture and uniformly mixed dough in the mixing operation are maintained in the range of from about 15°C to about 45°C; and
- 25           (d) extruding the uniformly mixed dough into a desired shaped piece, wherein the extrusion is carried out in conjunction with low specific mechanical energy and high pressure conditions, and under conditions such that the temperature of the uniformly mixed

dough in the extrusion operation is in the range of from about 40°C to about 100°C, and wherein said shaped piece is cohesive and maintains its shape when retorted.

5

2. A process according to claim 1 wherein the premixture comprises from about 15% to about 35% by weight protein, from about 25% to about 60% by weight starch, from about 1% to about 8% by weight fat choice white grease, from about 0.1% to about 1% by weight methionine, and from 0% to about 2% by weight dicalcium phosphate

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3. A process according to claim 2 wherein the premixture comprises from about 20% to about 40% by weight of a wheat gluten protein source and from about 30% to 75% by weight of a corn flour starch source.

15

4. A process according to claim 2 wherein the ratio of premixture to water is in the range of from about 1.65:1 to about 2.5:1.

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5. A process according to claim 4 wherein the secondary mixture is mixed in a paddle mixer for a period of time in the range of from about 3 minutes to about 8 minutes.

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6. A process according to claim 5 wherein the premixture further comprises from about 1% to about 30% by weight meat and bone meal.

7. A process according to claim 6 wherein the extruder is operated at a pressure of at least about 500 psig.

5 8. A process according to claim 7 wherein the specific mechanical energy of the extruder is in the range of from about 6 watt·hr./kg. to about 50 watt·hr./kg., wherein the extruder is operated at a speed in the range of from about 45 to about 60 RPM, and wherein the temperature of the dough  
10 exiting the extruder is in the range of from about 45°C to about 90°C.

9. A process for preparing a retort-stable, shaped food piece, said process comprising:

15 (a) preparing a premixture comprising

(1) from about 25% to about 35% by weight wheat gluten,

(2) from about 35% to about 65% by weight corn flour,

20 (3) from about 3% to about 6% by weight choice white grease,

(4) from about 0.2% to about 0.5% by weight methionine,

(5) from about 0.1% to about 1% by weight dicalcium phosphate;

25 (b) combining the premixture with water to form a secondary mixture, wherein the ratio of premixture

to water is in the range of from about 1.65:1 to about 1.85:1;

(c) mixing the secondary mixture in a ribbon mixer for a period of time in the range of from about 4 to about 6 minutes, thereby obtaining a substantially uniformly mixed dough, wherein said mixing is carried out under conditions such that the temperature of the secondary mixture and uniformly mixed dough in the mixing operation are maintained in the range of from about 20°C to about 25°C; and

(d) extruding the uniformly mixed dough into a desired shaped piece, wherein the extruder is operated at a speed in the range of from about 50 to 60 RPM, the dough exit temperature is in the range of from about 60°C to about 80°C, the exit pressure is at least 600 psig, and the specific mechanical energy provided by the extruder is in the range of from about 6 watt·hr./kg. to about 35 watt·hr./kg.

10. A retort-stable, shaped food piece prepared by the method comprising:

(a) preparing a premixture comprising

- (1) from about 15% to about 65% by weight protein,
- (2) from about 15% to about 65% by weight starch,
- (3) from 0% to about 9% by weight fat,
- (4) from 0% to about 0.7% by weight added sulfur,
- (5) from 0% to about 2% by weight dicalcium phosphate, wherein the weight percentage of the



premixture components are expressed as a percentage of the premixture;

(b) combining the premixture with water to form a secondary mixture, wherein the ratio of premixture to water is in the range of from about 1.6:1 to about 4:1;

(c) mixing the secondary mixture for a period of time sufficient to obtain a substantially uniformly mixed dough and under conditions such that the temperature of the secondary mixture and uniformly mixed dough in the mixing operation are maintained in the range of from about 15°C to about 45°C; and

(d) extruding the uniformly mixed dough into a desired shaped piece, wherein the extrusion is carried out in conjunction with low specific mechanical energy and high pressure conditions, and under conditions such that the temperature of the uniformly mixed dough in the extrusion operation is in the range of from about 40°C to about 100°C, and wherein said shaped piece is cohesive and maintains its shape when retorted.

11. A retort-stable, shaped food piece prepared by the method comprising:

(a) preparing a premixture comprising

(1) from about 25% to about 35% by weight wheat gluten,

- (2) from about 35% to about 65% by weight corn flour,
- (3) from about 3% to about 6% by weight choice white grease,
- 5 (4) from about 0.2% to about 0.5% by weight methionine,
- (5) from about 0.1% to about 1% by weight dicalcium phosphate;
- (b) combining the premixture with water to form a  
10 secondary mixture, wherein the ratio of premixture to water is in the range of from about 1.65:1 to about 1.85:1;
- (c) mixing the secondary mixture in a ribbon mixer for a  
15 period of time in the range of from about 4 to about 6 minutes, thereby obtaining a substantially uniformly mixed dough, wherein said mixing is carried out under conditions such that the temperature of the secondary mixture and uniformly mixed dough in the mixing operation are maintained  
20 in the range of from about 20°C to about 25°C; and
- (d) extruding the uniformly mixed dough into a desired shaped piece, wherein the extruder is operated at a speed in the range of from about 50 to 60 RPM, the dough exit temperature is in the range of from about  
25 60°C to about 80°C, the exit pressure is at least 600 psig, and the specific mechanical energy provided by the extruder is in the range of from about 6 watt·hr./kg. to about 35 watt·hr./kg.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/14028

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A23P1/12 A23K1/16 A23K1/18

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A23P A23K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,3 968 268 (LOUIS SAIR ET AL.) 6 July 1976 cited in the application see column 4, line 39 - column 5, line 23 see column 13, line 22 - line 26 see column 13, line 52 - column 14, line 34 see claims 1-22 --- -/--	1,10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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## INTERNATIONAL SEARCH REPORT

 Int'l. Application No  
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,4 015 026 (MORRIS P. BURKWALL ET AL.) 29 March 1977 see column 3, line 32 - line 54 see column 4, line 3 - line 40 see column 4, line 66 - column 5, line 13 see column 5, line 58 - line 61 see column 6, line 21 - line 50 see column 7, line 32 - line 51 see examples 1-3,6,7 see claims 1-4,6,7 ---	1,10
Y	GB,A,1 433 976 (THE QUAKER OATS COMPANY) 28 April 1976 see page 2, line 46 - line 65 see page 3, line 44 - line 70 see page 3, line 90 - line 98 see example 1 ---	1,10
A	US,A,4 524 081 (ARUN K. BANSAL) 18 June 1985 see column 4, line 61 - column 5, line 14 see claims 1-3 ---	1,2
A	JOURNAL OF FOOD SCIENCE, vol.57, no.6, 1992, CHICAGO US pages 1282 - 1284 N. UNKLESBAY ET AL. 'Thermophysical properties of extruded beef/corn flour blends' see page 1283; table 1 ---	1,10
A	EP,A,0 071 331 (RALSTON PURINA COMPANY) 9 February 1983 see claims 1-10 ---	1,10
A	US,A,3 965 268 (CHARLES T. STOCKER ET AL.) 22 June 1976 cited in the application see the whole document ---	1-11
A	US,A,4 419 372 (C. LAWRENCE GREENE ET AL.) 6 December 1983 see column 4, line 53 - column 5, line 22 see claims 1,7 ---	1
A	WO,A,93 05666 (NEW MEXICO STATE UNIVERSITY TECHNOLOGY TRANSFER CORPORATION) 1 April 1993 see page 6, line 8 - page 8, line 31 ---	1
3 A	EP,A,0 285 409 (THE QUAKER OATS COMPANY) 5 October 1988 see claim 10 -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/14028

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3968268	06-07-76	AU-A- 5939073 CA-A- 1019620 DE-A- 2343830 GB-A- 1439983 US-A- 3978244 US-A- 3978236	20-02-75 25-10-77 14-03-74 16-06-76 31-08-76 31-08-76
US-A-4015026	29-03-77	CA-A- 1067747	11-12-79
GB-A-1433976	28-04-76	BE-A- 824217 CA-A- 1035994 FR-A- 2274235 LU-A- 71622 NL-A- 7500230 SE-A- 7500285	09-07-75 08-08-78 09-01-76 09-12-75 16-12-75 15-12-75
US-A-4524081	18-06-85	US-A- 4542686	24-09-85
EP-A-0071331	09-02-83	CA-A- 1189741 JP-C- 1670757 JP-B- 3032343 JP-A- 58023751 CA-A- 1189740 JP-C- 1670758 JP-B- 3032344 JP-A- 58023752	02-07-85 12-06-92 10-05-91 12-02-83 02-07-85 12-06-92 10-05-91 12-02-83
US-A-3965268	22-06-76	NONE	
US-A-4419372	06-12-83	NONE	
WO-A-9305666	01-04-93	US-A- 5290584 AU-A- 2672192 US-A- 5283077	01-03-94 27-04-93 01-02-94
EP-A-0285409	05-10-88	US-A- 4791002 DE-D- 3885638 DE-T- 3885638 US-A- 4895731	13-12-88 23-12-93 19-05-94 23-01-90

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